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ZIRCONIUM-HAFNIUM SEPARATION:  
MIXER-SETTLER STUDIES

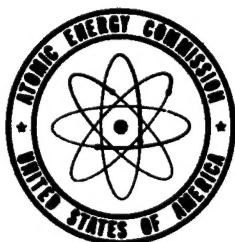
Final Report

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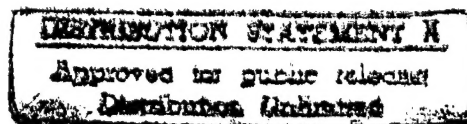
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ZIRCONIUM-HAFNIUM SEPARATION:  
MIXER-SETTLER STUDIES - FINAL REPORT

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June 6, 1950

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Operated by  
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## ABSTRACT

Use of the mixer-settler apparatus as a rapid means of determining improved conditions for plant operation is described including the experimental details.

The preparation of highly purified samples of both zirconium oxide and hafnium oxide is discussed.

(This document is concerned almost entirely with explorations of small scale continuous systems. Another document dealing with this general problem using small scale batch operations is being published simultaneously. It should prove of advantage to the reader to study this companion report, Document Y-611, by Barton, Overholser, and Grimes, to obtain a complete picture of the available information.)

ZIRCONIUM-HAFNIUM SEPARATION:  
MIXER-SETTLER STUDIES - FINAL REPORT

INTRODUCTION

The all glass mixer-settler apparatus, described in detail in Y-480<sup>1</sup> and Y-559<sup>2</sup>, was extensively used in the early experimental work on the separation of zirconium from hafnium. It had been demonstrated by actual plant operation that the data obtained from the mixer-settler could be applied directly to plant operations once sufficient correlation of both units had been made. Shortly after the zirconium plant was turned over to the production group (January, 1950), further work with the mixer-settler was begun. The experimental program planned and described herein had as its primary objectives the improvement of the plant process and the development of a procedure for producing pure hafnium oxide from the zirconium plant by-products. This work was carried out between January 23, and May 16, 1950. Studies were made to determine:

- (1) Under what conditions and to what degree the zirconium content of the feed might be increased.
- (2) How zirconium values might be reclaimed from the hexone effluent leaving the extraction column.
- (3) How raw material costs might be decreased.
- (4) Whether butyl acetate might be used as an additive to the organic phase to decrease the accumulation of solids in the columns.

- (5) Whether aging of the feed solution is necessary for development of the thiocyanate complex.

A practical plant procedure for the continuous production of low zirconium hafnium (about 200 ppm) was developed and some pure  $\text{HfO}_2$  prepared. A particular set of conditions was found which would, in the twelve stage mixer-settler, produce zirconium with a hafnium content of 0.075% and hafnium with a zirconium content of 10% simultaneously.

## EXPERIMENTAL

### Zirconium Studies

Standard Conditions. Run No. 40 (Table 1) was made to establish the results to be expected in the six stage mixer-settler when operated under standard plant conditions. For a considerable time during the period January through March 1950, the production group adopted operating conditions essentially as described below. Later, of course, when the pressing need for production volume was met, the production division made extensive experiments under other conditions. In this paper, standard plant conditions refers to those conditions prevalent during the period mentioned and described above. The aqueous feed solution was 1M in  $\text{ZrCl}_4$  and 1.34M in  $\text{NH}_4\text{CNS}$ . The organic phase was a 2M  $\text{HCNS}$  in hexone solution. The organic phase to aqueous phase volume ratio was four to one. The yield was 74% and the product contained 500 ppm hafnium compared to 1.5% hafnium in the feed. Under these conditions the production unit was maintaining essentially the same yield but with a hafnium content between 100-200 ppm.

Increased Production Rate. Efforts were made to effect a direct increase in the production rate by increasing the zirconium concentration of the feed and by decreasing the organic to aqueous volume ratio.

Four runs (Nos. 39, 42, 54, and 55) were made in which the zirconium concentration of the feed was substantially above the one molar standard plant concentration. Results of these runs indicated that it would not be possible to increase the zirconium concentration of the feed much above one molar without making a corresponding increase in the organic to aqueous volume ratio or perhaps increasing the HCNS concentration of the hexone to three molar or higher. If the organic to aqueous ratio must be increased in direct proportion to the increase in zirconium concentration, then no increase in production will result, since this increase in ratio can only be had by decreasing the aqueous rate as the production plant is now set up. It is not practical, for plant operation, to raise the HCNS concentration of the hexone to three molar or higher because such concentrations are very difficult to maintain under plant conditions. This is true because of the increased transfer of thiocyanate between organic and aqueous phases in both the extraction and stripping operations at these higher concentrations.

It was suggested to the authors that if a part of the free acid formed by the hydrolysis of  $ZrCl_4$  in the preparation of the plant feed were neutralized, a substantial increase in the distribution factor in favor of the organic phase and a corresponding possibility of reducing the organic to aqueous volume ratio might be realized. Three runs (Nos. 60, 61, and 62) were made to investigate this possibility. Feed for these

runs was prepared by adding to a  $\text{ZrCl}_4$  solution one mole of  $\text{NH}_4\text{OH}$  (as the concentrated reagent) for each mole of zirconium present. The feed was then made up in the standard manner and run with organic to aqueous volume ratios of 4:1; 2:1; and 3:2 with the results shown in Table 1. This procedure was tested in the production plant and gave satisfactory results.

Increased Yields. For some time it had been felt that there was a good possibility of increasing the yield of zirconium product in this process by stripping out a portion of the zirconium value in the hexone effluent from the extraction column. If this stripping solution is to be admitted directly to the extraction column at the feed point, then it must contain no substances which will interfere with the extraction process and the hafnium concentration of the contained oxides must not be appreciably higher than the hafnium concentration of the feed material. Only water and aqueous solutions of  $\text{HCl}$  and  $\text{NH}_4\text{CNS}$  were considered as possible stripping solutions. Since water and hydrochloric acid solution can be handled with proportioning pumps and require no mixing tanks or handling of solids, all the work on zirconium recovery was done with these solutions.

The hexone solutions of Zr-Hf thiocyanate for this work were removed from the zirconium production plant between the extraction and sulfuric acid scrubbing columns. The hafnium content of the contained oxides was in all cases about 8%. Conditions for and results obtained in these runs (Nos. 44, 47, 52, and 58) are shown in Table 1 in which it will be noted that in no case was the hafnium content of the contained oxides in the aqueous phase effluent appreciably greater than the approximately 2%



hafnium content of the zirconium plant feed material.

Before the two runs using hydrochloric acid for the stripping solution were made, one run (No. 50) was made under simulated multiple column conditions with the apparatus arranged as shown in Figure 1. A standard feed solution (1.4 M in  $\text{NH}_4\text{CNS}$  and 1 M in  $\text{ZrCl}_4$ ) was fed into stage seven. It was contacted with a 2M  $\text{HCNS}$  in hexone solution in six stages and the hexone effluent from this section of the apparatus was contacted with a stream of distilled water in six stages. The water solution of Zr-Hf thiocyanate was commingled with the feed solution at the feed point (stage seven). By this procedure, the hafnium content was reduced from about 2% in the feed to 0.2% in the product with a 94% yield.

Raw Material Cost Studies. The feasibility of using less sulfuric acid in the scrubbing column, of recovering thiocyanate values directly from the extraction column aqueous effluent (product), and of using less expensive forms of zirconium for feed material were investigated.

In normal plant operation the hexone effluent from the extraction column is scrubbed free of Zr-Hf thiocyanate with about 5N sulfuric acid at an organic to aqueous volume ratio of 4:1. In run No. 43, unscrubbed hexone from the production plant was scrubbed with 5N sulfuric acid in six stages at an organic to aqueous ratio of 9:1. The hexone was essentially free of zirconium and hafnium after three stages of extraction.

In the zirconium progress report Y-559<sup>2</sup> a procedure was described whereby the thiocyanate value of the product solution and the sulfuric acid scrub effluent could be recovered as a solution of ammonium

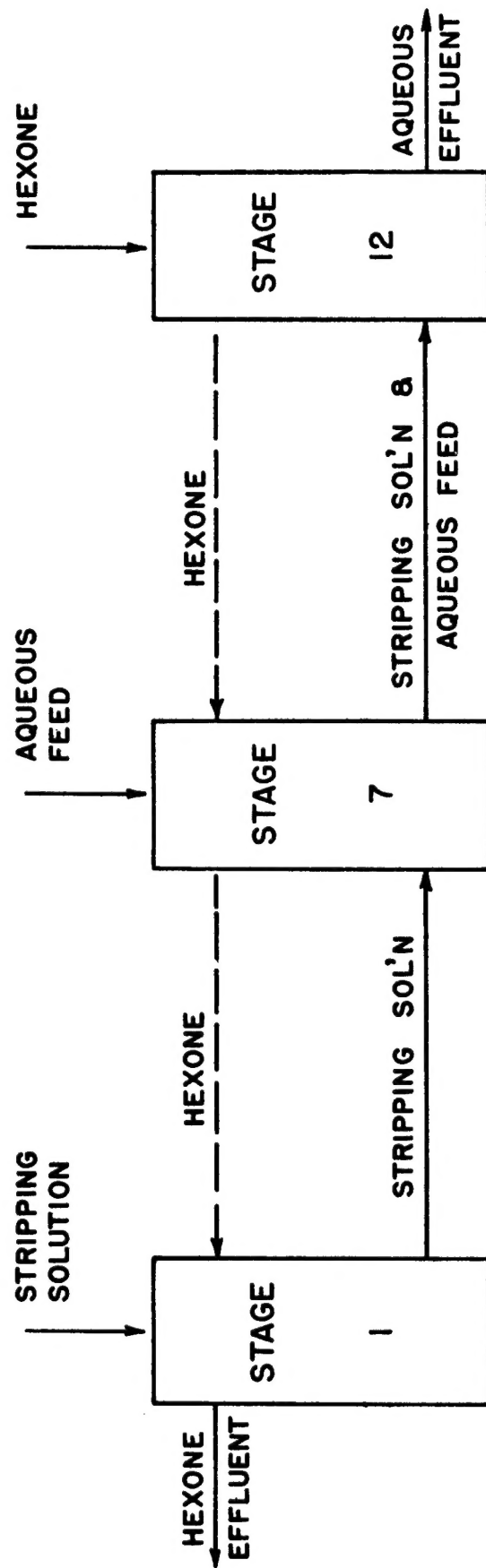


FIGURE I. COMPOSITE APPARATUS (two sections)

thiocyanate. Improvements in production procedures have eliminated this method from consideration. It was thought probable that considerable quantities of thiocyanate might be recovered from product effluents by direct extraction. To investigate this possibility, one run (No. 45) was made in which plant product solution was extracted with fresh hexone in six stages at an organic to aqueous volume ratio of 2:1. The aqueous feed (plant product solution) was 0.88M in thiocyanate while the aqueous effluent was 0.02M in thiocyanate giving a thiocyanate recovery of 97.7%. It was evident from the aqueous input and output rates, however, that a considerable amount (approximately 40%) of the aqueous phase was being carried along with the hexone and was discharged with the hexone effluent. This was not visually apparent, as the interfaces were all sharply defined.

Two runs (Nos. 48 and 51) were made to determine the feasibility of operating a stripping section and a thiocyanate recovery section along with the standard extraction section as a composite unit. In run No. 48 the apparatus was operated as such a composite system with six stages of extraction with hexone containing no thiocyanate followed by six stages in which the hexone was stripped by distilled water. Almost complete recovery of the thiocyanate was obtained, the aqueous effluent from the system running less than 0.01M in the thiocyanate. However, due to insufficient thiocyanate in the system, 99.25% of the input metals remained in the aqueous effluent, with no appreciable decrease in hafnium content.

In run No. 51, also, a standard zirconium feed solution was fed to the mid point of the apparatus. The feed was extracted in four stages

with a 2M HCNS in hexone solution followed by two stages of extraction with thiocyanate-free hexone. The hexone stripping solution was commingled with the hexone-thiocyanate extracting solution and the entire hexone effluent from the extraction section was stripped with distilled water in six stages (Figure 2). The aqueous effluent was 0.4M in thiocyanate, compared to a normal concentration of 0.85 to 0.9M. The yield was 91.6% of the input oxides with a hafnium content of 0.35%.

The results of this run definitely indicate that such a procedure should prove feasible for plant operation when a hexone regeneration system becomes available. The procedure would be to scrub the aqueous product solution with thiocyanate-free hexone and allow this hexone to enter the extraction column at the usual hexone feed point where it would be mixed with the extracting solution of hexone and thiocyanic acid. The hexone effluent from the sulfuric acid scrubbing column would be split into two streams; one would go to the hexone surge tank for reuse in the column and the other would go to the hexone regenerator for thiocyanate recovery. The aqueous phase from the sulfuric acid scrubber would be scrubbed free of thiocyanate with thiocyanate-free hexone and this organic phase would go directly to the hexone regenerator. Operation of the hexone regenerator would be as outlined in Y-559.

Since the thiocyanate recovered from hexone would be in the form of a concentrated solution of  $\text{NH}_4\text{CNS}$  in water, it was of interest to know if such a solution could be used to supply the needed thiocyanate directly to the system. In run No. 49 the organic phase was hexone containing no HCNS. To supply thiocyanate for the hexone, a concentrated solution of

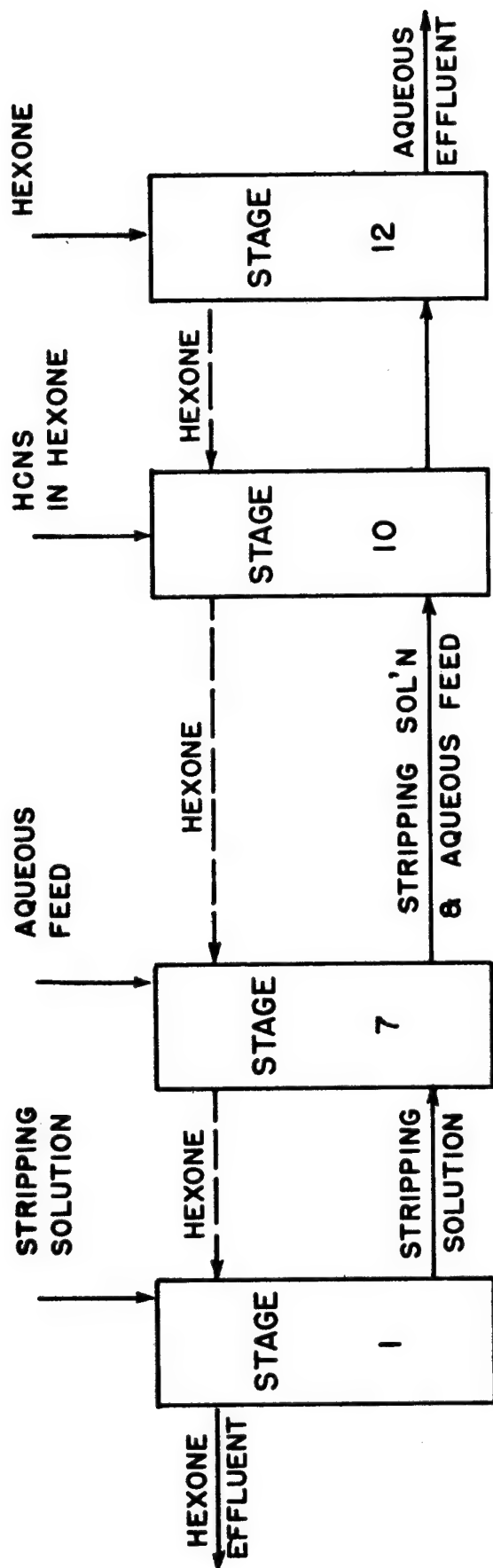


FIGURE 2. COMPOSITE APPARATUS (three sections)

$\text{NH}_4\text{CNS}$  was fed to the system two stages before the hexone feed point (Figure 3). It was intended that the hexone should extract the necessary thiocyanate from the  $\text{NH}_4\text{CNS}$  solution, but sufficient hydrogen ion was removed from the aqueous phase by extraction of  $\text{HCNS}$  that the pH rose to such a point as to precipitate zirconium hydroxide. When hydrogen ion was added to the concentrated  $\text{NH}_4\text{CNS}$  solution in a one to one mole ratio with the thiocyanate, the solution was stable only for a short period. No further runs of this type were made, but it is considered probable that by adding the required hydrogen ion, either in a separate stream at the  $\text{NH}_4\text{CNS}$  feed point or by addition to the zirconium feed solution, the system would operate in a satisfactory manner.

There had been some question as to whether aging of the Zr-Hf thiocyanate feed solution was necessary. Run No. 53 was made by feeding a  $\text{ZrCl}_4$  solution and an  $\text{NH}_4\text{CNS}$  solution into the six stage mixer-settler in such a manner that the mixed solutions yielded a standard feed solution. The fact that the product produced in this run was satisfactory proved that aging of the feed solution is unnecessary.

To serve as feed for the thiocyanate extraction plant, it is only necessary that the Zr-Hf mixture be dissolved in a chloride solution and be reasonably free from contaminants. The  $\text{ZrCl}_4$  thus far used in the plant is, therefore, not necessarily the cheapest source of zirconium for the process. Two runs were made using zirconium from other sources.

The zirconium feed for run No. 59 was extracted by Dr. C. J. Barton of this department from Baddeleyite ore supplied by the Brush Beryllium Company. Of the total oxides in the feed solution thus obtained, about

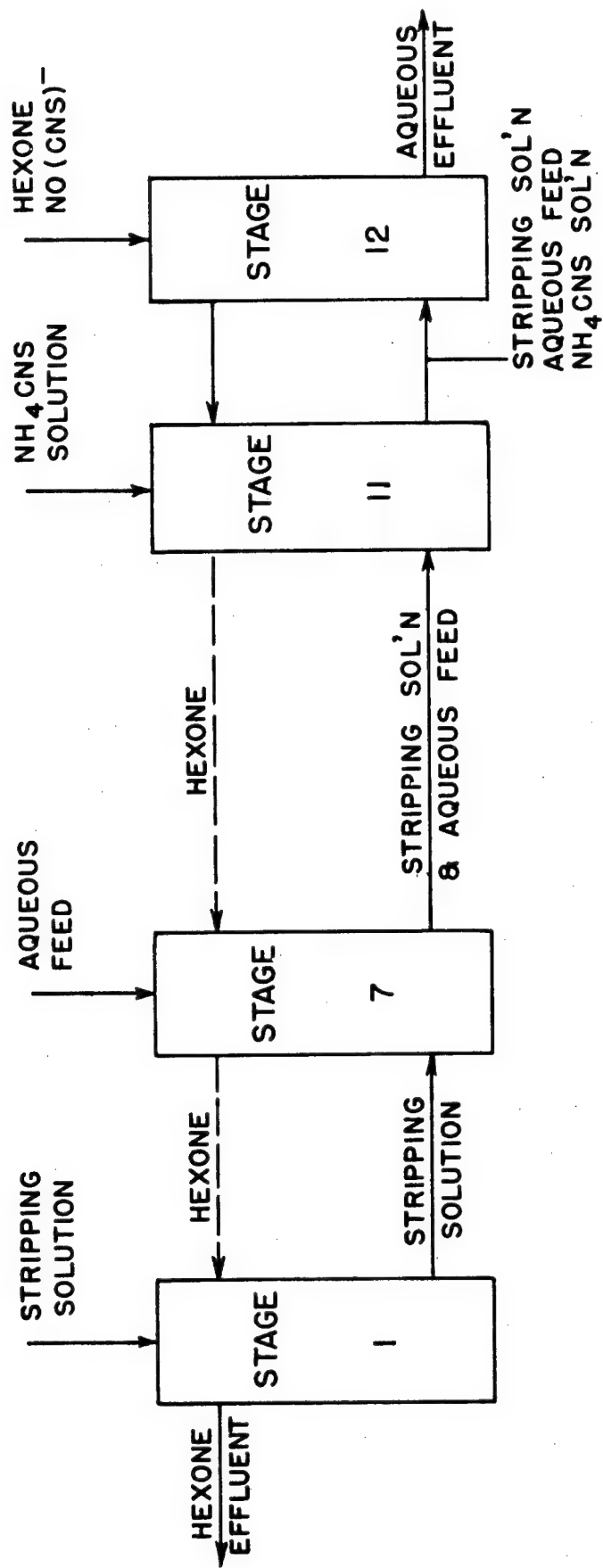


FIGURE 3. COMPOSITE APPARATUS (three sections)

90% was zirconium-hafnium oxides and the hafnium content was about 0.5%. The feed solution was only half molar in zirconium and one molar in thiocyanate. The run was normal in every respect and the zirconium product contained 100 ppm hafnium. The yield was 70.6%. Other impurities in the product are shown in Table 2.

A sample of hydrous zirconium-hafnium oxide was obtained from F. W. Berk and Company, Inc., Wood Ridge, New Jersey. This material is a white, free flowing solid readily soluble in concentrated hydrochloric acid with the evolution of considerable heat and requiring little additional heat to effect almost complete solution. The ratio of zirconium to chloride was adjusted to 1:3.75 with hydrochloric acid, which is about the ratio found in plant solutions resulting from the solution of  $ZrCl_4$  in water. With other conditions standard, a normal run was obtained in the six stage apparatus and the hafnium content was reduced from about 2% in the feed to 0.05% in the product with a yield of 67%. Other impurities after a salicylic acid precipitation of the product are shown in Table 2.

Reducing the Thiocyanate Decomposition. It was pointed out in Y-559 that solids arising from decomposition of thiocyanate in the extraction system resulted in flooding of the packed columns and necessitated frequent shutdowns for cleaning. The use of 20% butyl acetate-80% hexone as the organic phase allowed much longer periods of operation. In the unpacked columns now used in the production plant the problem is not so critical since the solids are eventually carried out of the system and continuous production can be maintained almost indefinitely. However,



these solids do seem to have a direct influence on the purity of the product and operation would be more uniform if they were not present. Two runs (Nos. 41 and 46) were made under standard conditions with the exception that the organic phase was 20% butyl acetate-80% hexone. In both cases the yields were about 75% while the hafnium content of the product was somewhat higher than that generally obtained under standard conditions. The indication was that under these specific conditions a somewhat lower yield would have to be accepted in order to produce satisfactory product.

An incidental result of adoption of the thiocyanate recovery system outlined above should be the reduction of solids in the system. This is true because the ammonium hydroxide scrub in the hexone regenerator will remove the solid decomposition products, as well as the thiocyanate, from the hexone.

Preparation of Pure Zirconium. A sample of product solution obtained from the zirconium production plant was twice passed through the mixer-settler (run No. 56) and the product was then precipitated with salicylic acid. This product contained no more than a trace of hafnium. Other impurities are shown in Table 2.

### Hafnium Studies

Background. The selective stripping of the hexone solution from the extraction cycle had a two fold purpose, (1) recovery and recycle of zirconium and (2) further enrichment of the hafnium by-product. The very early experiments quickly confirmed the feasibility of this program.

In run No. 52, for example, the oxides in the organic phase effluent were estimated by spectrographic analysis to contain only about 5% zirconium, plus relatively small amounts of other impurities, the remainder being hafnium. It was decided that whenever time was available from the zirconium problem that the mixer-settler would be used to develop a procedure for further concentrating the hafnium in the production plant tailings. Since hafnium tends to concentrate in the organic phase in the thiocyanate system, the final purification should be made by washing out the zirconium from an organic solution with an aqueous stripping solution. Only hydrochloric acid and sulfuric acid solutions were considered as practical stripping solutions for this work.

Preliminary Work. The first work on the hafnium problem had as its primary objective the preparation of a small amount of hafnium oxide with a low zirconium content using procedures which had already shown their ability to concentrate hafnium. As noted above, the stripping of a hexone solution of Hf-Zr thiocyanate with 0.5M hydrochloric acid is one such procedure, and one run was made utilizing this method. In this run (No. 57), sixty liters of unscrubbed hexone containing oxides running approximately 8% hafnium, were obtained from the zirconium production plant and passed through the twelve stage mixer-settler countercurrent to 0.5M hydrochloric acid at an organic to aqueous volume ratio of 2:1. The oxides remaining in the hexone effluent contained about 5% zirconium. This hexone solution was rerun against the 0.5M hydrochloric acid at an organic to aqueous volume ratio of 10:1. The oxides remaining in the hexone effluent from the second pass were about 2.5% zirconium.

Later, when it had been shown that two molar hydrochloric acid was perhaps a better stripping solution, one run (No. 63) was attempted under conditions which might be applicable to plant operations. For some time, the sulfuric acid effluent from the zirconium production plant was neutralized with sodium hydroxide and filtered to reclaim the hafnium value. A chloride solution prepared from some of this precipitate contained 172 grams of oxides per liter and was made 3 molar in ammonium thiocyanate. It was intended that this solution would be extracted in six stages with a two molar HCNS in hexone solution and the effluent hexone would be stripped with two molar hydrochloric acid in six stages. For some reason, never definitely established but quite probably due to silica in the aqueous feed, an emulsion was formed and the system failed to operate in a satisfactory manner. (The caustic precipitated plant tailings from which this feed was prepared had a high silica content.)

Since the aqueous and organic phases would separate satisfactorily on standing when using this caustic precipitated material, it was possible to obtain hexone solutions containing ten to fifteen grams of total oxides per liter by batch extracting an aqueous phase containing Hf-Zr thiocyanate with two molar HCNS in hexone. In runs No. 64 through 67, hexone solutions obtained in this manner were stripped in twelve stages with hydrochloric or sulfuric acid solutions of varied concentrations. Small amounts of product containing less than one percent zirconium were prepared but the yields were quite small and the results not reproducible. It was concluded that the 20 liters of hexone solution used in each of these runs was insufficient to establish equilibrium in the twelve stage apparatus

and the results, therefore, are not considered significant.

The original zirconium pilot plant, when no longer needed to produce zirconium, was used by the production division to concentrate some of the high hafnium material which had been recovered from the sulfuric acid scrubbing column in the production plant. Some of the product from the first of these runs was obtained and a hexone solution prepared from it. The hexone, containing 6.48 grams of total oxides per liter (of which about 85% was hafnium) and 2.2M in HCNS, was stripped in six stages with 2.7M hydrochloric at an organic to aqueous volume ratio of 10:1 (run No. 68). The yield was 77% of the total oxide input and the product was about 95% hafnium.

Six Stage Equilibrium Studies. Although the results obtained with hydrochloric acid stripping solutions were fairly good, other work<sup>3</sup> showed that the separation factor obtained when using sulfuric acid as the stripping solution was considerably higher than that obtained with hydrochloric acid.

Six runs (Nos. 69 through 74) were made in the six stage apparatus in each of which 20 liters of unscrubbed plant hexone was stripped with a solution of either hydrochloric or sulfuric acid at an organic to aqueous volume ratio of 10:1. In each case the fact that equilibrium was reached was established by a leveling off of the oxide concentration of the effluent stripping solution. The hafnium content of the oxides in the hexone probably varied between 25 and 35% and more or less inversely as the total oxide concentration. This variation in the hafnium concentrations accounts for most of the anomalous results.

Others may be accounted for by contamination of the mixer-settler with zirconium which will have a considerable influence in those cases in which the amount of product is small. As a result of these runs, 0.3M sulfuric acid was adopted as standard for further work.

It was thought that there might be a definite correlation between the concentration of the sulfate in the stripping solution and the amount of oxides it would extract. Two runs (Nos. 75 and 76) were made to check this possibility. In these runs, hexone solutions containing approximately 6 and 11 grams of total oxides per liter, respectively, were stripped with 0.3M sulfuric acid in six stages. The concentration of metals in the aqueous effluent increased roughly proportionately to the concentration of metals in the hexone feed. This indicates that the concentration of oxides in the aqueous stripping effluent is not controlled solely by the sulphate concentration.

A Practical Plant Procedure. Due to the very serious difficulties encountered in efforts to process the caustic soda precipitated hafnium concentrate from the zirconium plant, ammonium hydroxide was adopted as a precipitating agent. Approximately 50 pounds of the filter cake from the first ammonia precipitation were obtained, washed thoroughly, and dissolved in a minimum of hot concentrated hydrochloric acid. The hafnium content was about 27% of the total oxides. Three runs (Nos. 77, 79 and 81) were made with this solution under conditions which could be scaled up to handle any amount of hafnium concentrate which may become available.

The mixer-settler was arranged to provide two six stage sections, one for extraction and one for stripping as shown in Figure 4.

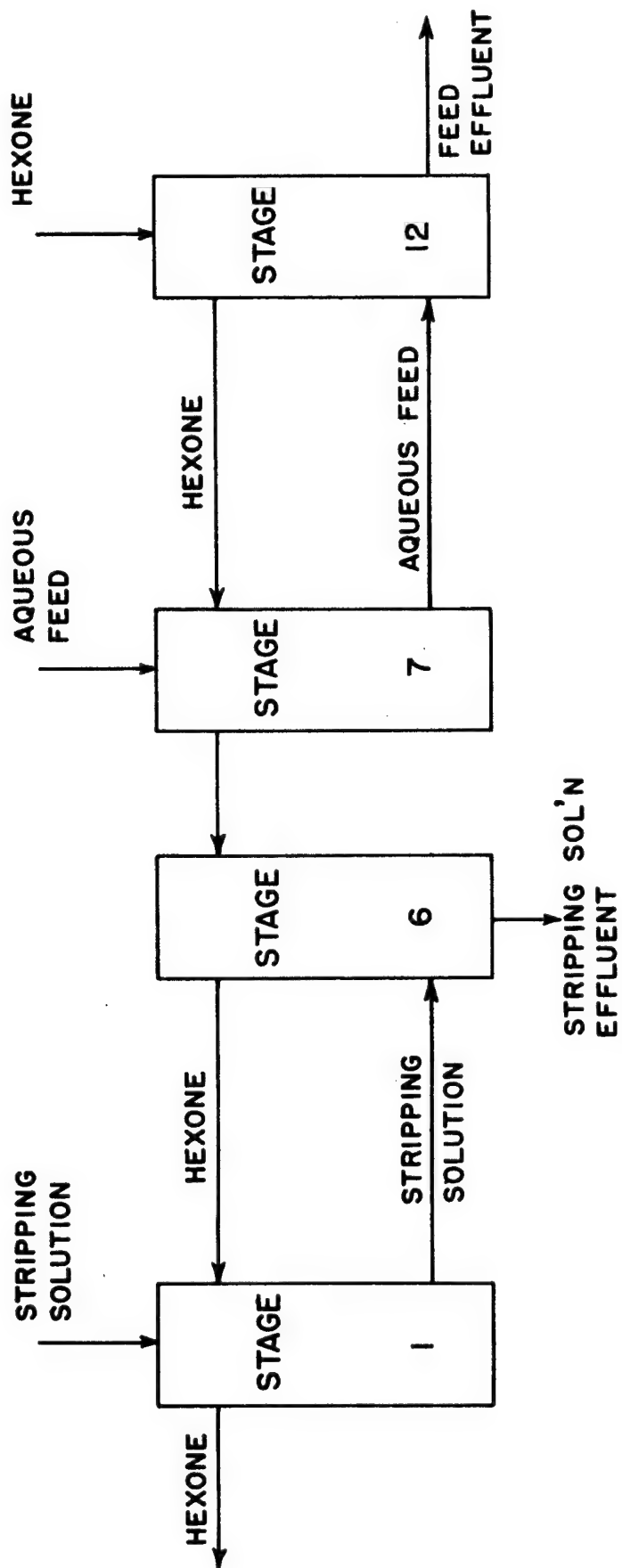


FIGURE 4. TWO SIX STAGE SECTIONS

The first of the runs (No. 77) was made with an organic to aqueous feed volume ratio of 4:1 and an organic to sulfuric acid volume ratio of 5:1. The product was very good (about 0.05% Zr), but the yield was only 52% of the input hafnium. For the second of these runs (No. 79) the organic rate was increased to give an organic to aqueous-feed volume ratio of 6:1 and a correspondingly increased organic to sulfuric acid volume ratio of 7.5:1. The yield was increased to 81% based on the input hafnium while the zirconium content of the product was about 0.5%. Run No. 81 was made using the same conditions as a check on run No. 79 and gave essentially the same results.

Run No. 80 was made to determine if the hafnium value of the sulfuric acid stripping solution could be reclaimed much as zirconium values are reclaimed by stripping the hexone with hydrochloric acid in the production plant. The 0.3M sulfuric acid effluent from run No. 79 was 2.07M in thiocyanate and contained 76.0 grams of oxide per liter of which 5% was hafnium. This solution was stripped in six stages with a 1.9M HCNS in hexone solution at an organic to aqueous volume ratio of 5:1. The hexone effluent contained about 45% of the total oxides of which about 10% was hafnium or a recovery of roughly 90% of the input hafnium. Under good conditions, it appears that most of the hafnium value could be reclaimed from such solutions.

There had accumulated in this laboratory from various mixer-settler runs about 135 grams of material between 90 and 95% hafnium. This material was dissolved in a minimum of hot concentrated hydrochloric acid, diluted to five liters and  $\text{NH}_4\text{CNS}$  added to bring it to a 2M thiocyanate

concentration. This feed solution was extracted (run No. 78) by a 1.9M HCNS in hexone solution in six stages at an organic to aqueous ratio of 4:1 and the effluent hexone was stripped in six stages with 0.3M sulfuric acid at an organic to aqueous volume ratio of 10:1. The yield was 94% based on the input hafnium and the zirconium content of the product was estimated at 200 ppm by spectrographic analysis. This appears to be about the limit of purity to be expected from this mixer-settler due to zirconium contamination.

The Zirconium-Hafnium Plant. Although it has been demonstrated that hafnium containing less than one percent zirconium can be produced from a 30% hafnium-70% zirconium mixture with reasonably good yield, it is evident that both purity and yield will vary directly with the concentration of hafnium in the zirconium plant tailings used for feed material. With this in mind a set of conditions was selected which it was believed might substantially increase the zirconium yield and consequently the hafnium concentration of the plant tailings, and would be applicable to plant operation. In run No. 82 the twelve stage mixer-settler was operated as a composite apparatus. The aqueous feed was prepared by adding one mole of ammonium hydroxide for each mole of zirconium present to a zirconium tetrachloride solution. This solution was then made up to standard plant concentrations and fed to the mid point of the apparatus. It was extracted in six stages with 2.2M HCNS in hexone at an organic to aqueous volume ratio of 5:1. The hexone effluent from the extraction section was stripped in six stages with a four molar hydrochloric acid solution at the standard plant organic to hydrochloric acid ratio of 10:1.



The stripping solution effluent then entered the extraction section along with the feed. It was believed that these conditions would more evenly distribute the extraction load between the two sections. The aqueous effluent contained about 99.8% of the input zirconium and had a hafnium content of 750 parts per million. The organic phase contained 96.3% of the input hafnium and had a zirconium content of 10%. Very recently another column was added to the zirconium production plant for the purpose of reducing the hafnium content of the zirconium product below 100 ppm. With this extra column and somewhat altered conditions it is quite possible that the hafnium concentration of the tailings may be substantially increased while the hafnium content of the zirconium product is maintained at a very low figure.

#### Preparation of Hafnium Oxide Using Standard Laboratory Equipment.

The preparation of essentially pure hafnium oxide can no longer be considered a very difficult task even when no special equipment is available. This fact is effectively demonstrated by two cases in which batch shake-outs using a separatory funnel were used to concentrate hafnium oxide.

A sample of zirconium and hafnium hydrous oxides which contained about 25% hafnium oxide was obtained from the zirconium pilot plant. The sample was dissolved in HCl,  $\text{NH}_4\text{CNS}$  was added, and about half the metal value was extracted into a hexone solution about two molar in HCNS. This hexone solution was then extracted four times with one-half its volume of 0.2 molar sulfuric acid. After these extractions the hexone yielded a small amount of oxide which contained about 0.4% zirconium.

It appeared that the ultimate purity of hafnium oxide produced in the mixer-settler was limited by zirconium contamination because of the difficulty of cleaning such a complicated all-glass apparatus. In an effort to prepare essentially pure hafnium oxide, the product from run No. 81 was subjected to further purification using new, standard, glass apparatus. This material was contaminated with about 0.5% zirconium and about 0.25% titanium plus lesser amounts of other elements.

The first problem was removal of the titanium. A number of possible precipitations were made as shown in Table 3. Of these, the crystallization from nine molar HCl was the most effective; also the crystals could be redissolved in water and no ignition step was necessary. The solution obtained by dissolving these crystals was partially neutralized with  $\text{NH}_4\text{OH}$ , made approximately two molar in  $\text{NH}_4\text{CNS}$ , and extracted with four 250 ml portions of hexone which was two molar in  $\text{HCNS}$ . The extractions were made in a two liter separatory funnel. The four portions of hexone were combined and extracted ten times with 50 ml portions of 0.3 molar sulfuric acid and each fraction was held separately, precipitated with  $\text{NH}_4\text{OH}$ , filtered, and ignited in platinum. The residual material in the hexone was recovered by extracting twice with 50 ml portions of approximately 20% sulfuric acid. This sulfate solution was ammonia precipitated, filtered, and washed reasonably free of sulfate. The precipitate was redissolved in HCl, crystallized from nine molar HCl, filtered, and washed with nine molar HCl. The filtrate and wash acid were combined, precipitated with  $\text{NH}_4\text{OH}$ , filtered, redissolved in hydrochloric acid and precipitated with salicylic acid. Both fractions of

final product were ignited in porcelain. The chloride crystallization yielded about two grams and the salicylic acid precipitate yielded about three grams of oxide. The purity of this material was established by spectrographic analysis and is shown in Table 2.

#### SUMMARY

Extensive additional experiments in the all-glass mixer-settler have been made in an effort to improve the efficiency of the zirconium production process as well as to further correlate the mixer-settler data with plant operations. The work has brought out many points among which are:

1. The concentration of zirconium in the feed solution cannot be increased materially above 1 or 1.25 molar and still maintain the same separation efficiency in a given column design.
2. It was demonstrated that a scrubbing solution of 2 molar hydrochloric acid could be used to recover substantial quantities of zirconium from the hexone solution emerging from the extraction phase. This scrubbing solution was recycled to the extraction stage thereby substantially increasing the zirconium recovery and increasing the hafnium content of the by-product.
3. Two other sources of zirconium feed material were investigated and found to be entirely suitable for standard processing if the need arises.
4. It was demonstrated that substantial reduction in consumption of

sulfuric acid in the scrubbing stage could be effected if desired.

5. Use of 20:80 volume ratio butylacetate:hexone was investigated further and found to give slightly less separation than 100% hexone under normal operating conditions.

6. The adaptation of the hexone-thiocyanate system for the preparation of pure hafnium was investigated and several samples containing in excess of 99% hafnium oxide prepared.

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Table

Mixer Settler

## INFLUENTS

Run Number	Aqueous Phase				Organic Phase (a)			Stripping Sol'n	
	Zirconium Concentration	Hafnium Concentration (g)	Thiocyanate Concentration (Molar)	Flow Rate (ml/min)	Total Oxides (g/l)	Thiocyanate Concentration (Molar)	Flow Rate (ml/min)	Type	Flow Rate (ml/min)
39	1.5 M	2	1.0	20	-	3.0	120	-	-
40	1.0 M	2	1.3	20	-	2.1	80	-	-
41	1.0 M	2	1.5	20	-	2.0(b)	80	-	-
42	1.4 M	2	1.7	20	-	1.9	120	-	-
43	-	8	-	-	8.46	2.1	100	4.9 M H <sub>2</sub> SO <sub>4</sub>	11
44	-	8	-	-	9.24	2.1	96	H <sub>2</sub> O	12
45	0.74 M	0.2	0.88	130	-	0	70	-	-
46	1.0 M	2	1.5	21	-	1.9(b)	87	-	-
47	-	8	-	-	8.9	2.1	100	H <sub>2</sub> O	33
48	1.0 M	2	1.45	18	-	0	52	H <sub>2</sub> O	7
49	Zirconium hydroxide precipitated				-	-	-	-	-
50	1.0 M	2	1.44	13	-	2.1	56	H <sub>2</sub> O	19
51	Described in text				-	-	-	-	-
52(e)	-	8	-	-	10.3	2.1	50	0.5 M HCl	23
53(d)	1.0 M	2	1.5	20	-	1.9	80	-	-
54	1.25 M	2	1.5	20	-	2.0	80	-	-
55	1.25 M	2	1.85	20	-	2.0	80	-	-
56	0.7 M	0.015	1.0	20	-	2.1	80	-	-
56(f)	(g)	0.005	(g)	20	-	2.0	80	-	-
57	-	8	-	-	unscrubbed plant hexane		100	0.5 M HCl	50
57(f)	-	95	-	-	(g)	(g)	100	0.5 M HCl	10
58	-	8	-	-	9.7	2.3	100	2 M HCl	10
59	0.5 M	0.5	1.0	20	-	2.1	80	-	-
60(e)	1.0 M	2	1.6	20	-	2.1	80	-	-
61(e)	1.0 M	2	1.5	40	-	2.0	80	-	-
62(e)	1.0 M	2	1.4	20	-	1.75	90	-	-
63	Emulsified				-	-	-	-	-
64-67	Twelve stage runs in which equilibrium was not attained				-	-	-	-	-
68	-	90	-	-	6.5	2.2	80	2 M HCl	8
69	-	30	-	-	2.1	2.5	80	0.15 M H <sub>2</sub> SO <sub>4</sub>	8
70	-	30	-	-	1.5	2.6	80	0.3 M H <sub>2</sub> SO <sub>4</sub>	8
71	-	30	-	-	1.8	2.3	80	1 M H <sub>2</sub> SO <sub>4</sub>	8
72	-	30	-	-	2.8	2.4	80	0.75 M H <sub>2</sub> SO <sub>4</sub>	8
73	-	30	-	-	3.1	2.6	80	2.3 M HCl	8
74	-	30	-	-	2.1	2.5	80	4.4 M HCl	8
75	-	30	-	-	6	2.2	80	0.5 M H <sub>2</sub> SO <sub>4</sub>	8
76	-	30	-	-	10.9	2.2	80	0.3 M H <sub>2</sub> SO <sub>4</sub>	8
77	105.5 g/l oxide	27	1.92	20	-	2.3	80	0.3 M H <sub>2</sub> SO <sub>4</sub>	16
78	26.9 g/l	92	2.0	20	-	1.9	120	0.3 M H <sub>2</sub> SO <sub>4</sub>	16
79	116.9 g/l	27	1.8	20	-	2.3	120	0.3 M H <sub>2</sub> SO <sub>4</sub>	16
80	76.9 g/l	5	2.02 + 0.3 M H <sub>2</sub> SO <sub>4</sub>		-	1.9	100	-	-
81	121 g/l	27	1.8	20	-	1.8	120	0.3 M H <sub>2</sub> SO <sub>4</sub>	16
82(e)	1.0 M	2	1.5	20	-	2.2	100	4 M HCl	10
83	1.0 M	2	1.5	20	-	2.0	80	-	-

(a) Hexane unless otherwise noted.

(b) Mixture of 20% butyl acetate and 80% hexane.

(c) Twelve stage run. Other simple extraction runs were six.

(d) Aqueous feed solution was formed by mixing ZrCl<sub>4</sub> and NH<sub>4</sub>Cl.

(e) The free acid in the aqueous feed was partially neutralized.

(f) Second pass of previous run.

(g) Product from first pass.

Table 1

## Mixer Settler Run Data

Leaching Sol'n		EFFLUENTS								
		Aqueous Phase			Organic Phase			Stripping Solution		
Flow Rate (ml/min)		Yield, as Total Oxides (\$)	Hafnium Content (\$)	Yield of Hafnium (\$)	Yield, as Total Oxides (\$)	Hafnium Content (\$)	Yield of Hafnium (\$)	Yield, as Total Oxides (\$)	Hafnium Content (\$)	Yield of Hafnium (\$)
-	-	70	0.05	-	-	-	-	-	-	-
-	-	74	0.05	-	-	-	-	-	-	-
-	-	75	0.1	-	-	-	-	-	-	-
-	-	78	0.1	-	-	-	-	-	-	-
SO <sub>4</sub>	11	Scrubbing was complete			-	-	-	51	2	-
-	12	-	-	-	Aqueous phase was stripped free of thiocyanate			-	-	-
-	-	63	0.1	-	-	-	-	-	-	-
-	-	62	0.05	-	-	-	-	-	-	-
-	33	87	1.0	-	-	-	-	-	-	-
-	7	99.25	2	-	0.25	30	-	Commingled with aqueous feed.		
-	19	94	0.2	-	-	-	-	Commingled with aqueous feed.		
1	23	94	2	-	6	~ 95	-	-	-	-
-	-	74	0.05	-	-	-	-	-	-	-
-	-	90	0.75	-	-	-	-	-	-	-
-	-	80	0.2	-	-	-	-	-	-	-
-	-	69	0.005	-	-	-	-	-	-	-
-	-	-	< 0.005	-	-	-	-	-	-	-
1	50	-	~ 95	-	-	-	-	-	-	-
1	10	-	97.5	-	-	-	-	-	-	-
1	10	98	2	-	-	-	-	-	-	-
-	-	73	0.01	-	-	-	-	-	-	-
-	-	40	0.05	-	-	-	-	-	-	-
-	-	60	0.075	-	-	-	-	-	-	-
-	-	70	0.1	-	-	-	-	-	-	-
1	8	-	-	-	79	95	94.7	21	20	5.3
SO <sub>4</sub>	8	-	-	-	56	50	-	44	-	-
SO <sub>4</sub>	8	-	-	-	47	99 +	-	53	-	-
SO <sub>4</sub>	8	-	-	-	6	99 +	-	94	-	-
SO <sub>4</sub>	8	-	-	-	23	99 +	-	77	-	-
1	8	-	-	-	47	40	-	53	-	-
1	8	-	-	-	43	95	-	57	-	-
SO <sub>4</sub>	8	-	-	-	30	95	-	70	-	-
SO <sub>4</sub>	8	-	-	-	42	95	-	58	-	-
SO <sub>4</sub>	16	25	15	14	14	~ 400 ppm Zr	52	61	15	34
SO <sub>4</sub>	16	0	0	0	93.7	200 ppm Zr	94	6.3	80	5
SO <sub>4</sub>	16	21	10	8	21	99.5	81	58	5	11
-	-	56	1	12	44	10	88	-	-	-
SO <sub>4</sub>	16	23	18	16	19	99.5	73	59	5	11
1	10	98	0.075	3.7	2	90	96.3	Commingled with aqueous feed.		
-	-	67	0.05	-	-	-	-	-	-	-

runs were six stages.

ZrCl<sub>4</sub> and NH<sub>4</sub>OH solutions in the first stage of the apparatus.  
ally neutralized with NH<sub>4</sub>OH.

Table 2

Purity of Product Based on Spectrographic Analysis

Element	Zr Oxide Run # 56	Zr Oxide from Baddeleyite Run # 59	Zr Oxide F.W.Berk & Co. Run # 83	Hafnium Oxide Batch Extractions	
				HCl Crys.	Salic.
Al	<10*	>1000	<10	<10	< 10
B	2	10	3	0.2	1
Ba		40	<10	<10	< 10
Be	<0.02	>10	< 0.02	< 0.02	< 0.02
Ca	<10	500	20	20	20
Cd	< 2	< 2	< 2	< 2	< 2
Co	<10	<10	<10	<10	< 10
Cr	< 4	40	< 4	4	4
Cu	15	4	10		
Fe	<10	>1000	40	<10	< 10
Hf	<150**	<250	-	-	-
Li	<100	<100	<100	<100	<100
Mg		200	< 10	10	10
Mn	< 1	>1000	2	< 1	< 1
Mo	10	30	< 10	< 10	< 10
Na	<100	< 100	<100	<100	<100
Ni	15	30	40	10	10
P	200	4000	400	<100	<100
Pb	< 10	40	< 10	< 10	< 10
Si	200	500	40	100	100
Sn	< 10	< 10	< 10	< 10	< 10
Ti	< 4	>1000	>1000	4	100
V	< 10		< 10	< 10	< 10
Zn		<100	<100	<100	<100
Zr	-	-	-	200	200

\* Results are in parts per million.

\*\* Estimated at less than 50 parts per million.

Note: Run No. 59 received an ammonia precipitation; Run No. 56 and Run No. 83 both received purification by precipitation as salicylate.



Table 3Comparison of Procedures for Freeing Hafnium of Titanium

<u>Method</u>	<u>% Ti in Pp't</u>	<u>App. Yield</u>
Precipitation with $\text{NH}_4\text{OH}$	0.25	100%
Precipitation with n-butyl arsonic acid <sup>(a)</sup>	0.02	90-100
Precipitation with salicylic acid	0.25	100
Precipitation with salicylic acid in 3% $\text{H}_2\text{O}_2$	-	0
Precipitation with phthalic acid	0.25	98
Precipitation with phthalic acid in 3% $\text{H}_2\text{O}_2$	0.15	45
Crystallization from 9M $\text{HCl}$	0.005	75
Crystallization as the basic sulfate <sup>(b)</sup>	0.02	Approaches 100% on long standing

(a) Giest and Chandlee, Ind. Eng. Chem., Anal. Ed., 9, 169 (1937)

(b) Otto Hauser, Z. Anorg. Chem. 54, 196-212 (1907)